

# Observation of superconducting gap in boron-doped diamond by laser-excited photoemission spectroscopy

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## Abstract

We have investigated the low energy electronic state of a boron-doped diamond thin film by the ultrahigh resolution laser-excited photoemission spectroscopy. We observed a clear shift of the leading edge below 11 K indicative of a superconducting gap opening ( $\Delta \sim 0.78$  meV at 4.5 K). The gap feature is significantly broad and the well-defined quasiparticle peak is not recognizable even at the lowest temperature of measurement 4.5 K. We discuss our result in terms of possible disorder effect on superconductivity in this system.

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Diamond has been well studied through the progress of solid state physics as one of the simplest  $sp^3$  covalent system. Although it is a typical band insulator with a gap of 5.5 eV, its high thermal conductivity owing to the high Debye temperature is well known also from the application point of view. When doped with boron (B), which plays a role of an acceptor with the activation energy of 0.37 eV, the diamond behaves as a well organized  $p$ -type semiconductor. On increasing the B concentration ( $n_B$ ), the system goes across the insulator-metal (Mott) transition at  $n_B^{\text{MI}} \sim 2 \times 10^{20} \text{ cm}^{-3}$ . It is recently that a striking discovery of the superconductivity ( $T_c \sim 2 \text{ K}$ ) was reported in B-concentration above  $n_B^{\text{MI}}$  [1]. Shortly after, by virtue of advanced crystal growth technique such as the chemical vapor deposition (CVD) method, the sample quality and its  $T_c$  have become higher [2, 3, 4, 5]. Such progress has made possible the experimental studies in a wide variety, and opens a new field for device applications using diamond related materials.

From the theoretical side, several scenarios have been proposed. The band calculations with the virtual crystal approximation (VCA) [6, 7] predict that the top of the host diamond valence band at  $\Gamma$ -point is shifted above the Fermi level in the metallic region (*e.g.* 0.61 eV shift for 2.5% hole doping in [7]). The holes at the small pocket around  $\Gamma$  strongly couple to the optical phonon with  $\sim 160 \text{ meV}$ , which gives rise to the BCS-type superconductivity. Actually, the rigid shift of the valence band and the phonon softening at  $\Gamma$ -point are recently confirmed by the angle-resolved PES [8] and inelastic x-ray [9] measurements respectively, which shows that the above models are valid at least qualitatively. The supercell calculation points out a certain importance of the boron circumstance in addition, which has a large local density-of-states (DOS) at  $E_F$  (though smaller than the total DOS of carbon) and modifies the host diamond band by its randomness [10, 11]. They also show that the local B-C vibration mode will significantly contribute to the electron-phonon coupling constant  $\lambda$ . On the contrary, there is a theoretical report which is entirely based upon the half-filled narrow boron impurity band as schematically realized in the Mott transition picture [12]. This scenario will produce a dirty superconducting state with an extended  $s$ -wave gap by an exotic pairing interaction, resonating-valence-bond (RVB) mechanism, which manifests itself in a strong correlation regime.

In this study, we investigated the low-energy electronic structure of the B-doped diamond to clarify the characteristics of the superconductivity realized in this doped semiconductor system. By using the ultrahigh resolution laser-excited photoemission spectroscopy, we

succeeded in the observation of the superconducting gap evolving below 11 K. We discuss our result in the light of boron-induced disorder effect.

PES measurements were performed using a system constructed with the Scienta R4000 electron analyzer and an ultraviolet ( $h\nu = 6.994$  eV) laser for the incident light [13]. The escape depth of the photoelectron in this energy region (*i.e.* kinetic energy of  $2 \sim 3$  eV) attains a large value of  $\sim 100$  Å, [14] which enables us the bulk-sensitive measurements. The temperature was precisely controlled down to 4.5 K using a flow-type He liquid refrigerator. The base pressure of the chamber was below  $\sim 5 \times 10^{-11}$  Torr throughout all the measurements. We annealed the samples before the measurement at 400 °C in the vacuum of  $< 10^{-7}$  Torr. This procedure increased the photoelectron intensity near the Fermi level ( $E_F$ ) for about a factor of 10 times, while not changing the spectral shape. Since we could not catch clear evidence of angle-resolved ( $k$ -dispersed) signal, all measurements were performed with an angle-integration mode. The energy resolution was  $\Delta E = 0.7$  meV. The Fermi level ( $E_F$ ) of the sample was referred to that of the Au film evaporated on the sample substrate.

The B-doped diamond (BDD) sample we used for our measurement is obtained by a microwave plasma-assisted chemical vapor deposition (CVD) method as described elsewhere [2, 5]. It was grown homoepitaxially on an undoped (1 1 1) oriented diamond synthesized in high pressure and high temperature [5]. The BDD thus grown is single crystalline. The boron concentration determined by the secondary ion mass spectroscopy method is  $n_B = 8.4 \times 10^{21} \text{ cm}^{-3}$ , which corresponds to B/C ratio of 5%. The carrier density estimated from the Hall coefficient is  $n_H = 1.3 \times 10^{22} \text{ cm}^{-3}$  [5]. We show in Fig. 1 the resistivity and magnetization curves for the BDD sample. The superconducting transition temperature of this sample determined from the Meissner response is  $T_c^m = 6.6$  K as indicated in the inset of Fig. 1(b). The diamagnetic response keeps increasing on lowering the temperature down to 2 K without any sign of saturation, reflecting the disordered nature of the superconductivity. The resistivity, on the other hand, steeply starts decreasing at 8.2 K and shows the zero-resistivity at around 7 K. There is another characteristic temperature  $T_0 \sim 11$  K where the resistivity starts to deviate from that of the weakly insulating normal state under the magnetic field, which will be discussed later. The normal-state resistivity is almost temperature-independent with the values of  $\rho(300\text{K}) = 0.59 \text{ m}\Omega$  (not shown) and  $\rho(10\text{K}) = 0.68 \text{ m}\Omega$ , indicative of the fairly localized carrier dynamics in this system. Here

we estimate the carrier mean free path from  $l = \frac{\hbar k_F \tau}{m^*} = \frac{\hbar k_F}{ne^2 \rho}$  and  $k_F = (3\pi^2 n)^{1/3}$  in a simple free-electron picture. Substituting  $\rho(10\text{K})$  and the above mentioned  $n_H$  for the carrier density  $n$ , we obtain  $l = 3.4 \text{ \AA}$ . It is nearly equivalent with the cubic lattice parameter  $a = 3.57 \text{ \AA}$  [5] indicating that this system is fairly close to the Mott-Ioffe-Regel limit [15]. We also note that this value coincides with that previously reported by Sidorov *et al.* in a lower-doped single crystalline sample ( $n_H \sim 1.8 \times 10^{21} \text{ cm}^{-3}$ ,  $\rho(10\text{K}) \sim 2.5 \text{ m}\Omega\text{cm}$ ) [16]. Since  $k_F$  is greater in our sample with higher  $n$ , the carrier mobility  $\mu = \frac{e\tau}{m^*}$  must be lower instead in order to obtain the same  $l$ , where  $\tau$  and  $m^*$  represent the lifetime and the effective mass of the carriers. On the other hand, the coherence length estimated from the upper critical field  $H_{c2}$  is  $\xi \sim 60 \text{ \AA} > l$  [5], which classifies this BDD sample as a dirty superconductor.

Figure 2 shows the photoelectron spectrum (PES) of the superconducting state observed in the BDD sample. With decreasing temperature from 15.5 K, a slight shift of the spectral edge can be observed below 9.5 K (see the enlarged plot in Fig. 2(b)). At the same time, the spectral shape becomes slightly convex downward at  $E_F$ . Such temperature dependence is indicative of a gap opening at  $E_F$ , which is a clear evidence of the mass superconductivity in this sample. Even at the lowest temperature (4.5 K), however, a considerable amount of DOS at  $E_F$  remains and a clear quasiparticle peak cannot be observed. We tried to estimate the gap value at 4.5 K by fitting the PES using the Dynes function [17] for the DOS represented with the isotropic (*s*-wave) superconducting gap and the phenomenological broadening parameters  $\Delta$  and  $\Gamma$ , as

$$D(E_B, \Delta, \Gamma) = \text{Re} \frac{E_B - i\Gamma}{\sqrt{(E_B - i\Gamma)^2 - \Delta^2}} .$$

The best-fitted result is shown in Fig. 2(c) as the red curve, with the parameters  $\Delta = 0.78 \text{ meV}$  and  $\Gamma = 0.7 \text{ meV}$ . We note that  $\Gamma$  is remarkably large,  $\Gamma \approx \Delta$ , which accounts for the large DOS at  $E_F$  and the hardly recognizable quasiparticle peak. Due to such spectral shape, it is impossible at present to discuss the superconducting gap symmetry, whether it is simple *s*-wave or not, solely from our result. Here we estimate the reduced gap  $\Delta(0)/k_B T_c$  from our result at the lowest temperature, ie.  $\Delta(4.5\text{K}) = 0.78 \text{ meV}$ , by simply assuming the BCS-like temperature dependence of  $\Delta(T)$ . If we take  $T_c = T_c^m = 6.6 \text{ K}$ ,  $\Delta(0)/k_B T_c = 1.78$  is obtained with  $\Delta(0) = 1.01 \text{ meV}$ . It is close to a typical value for weakly-coupled BCS superconductors. This result thus seems to suggest that  $\Delta$  we observed is well related in a weak-coupling regime with  $T_c^m$  where the superconductivity shows up in the volume-sensitive

magnetization.

To confirm the evolution of the gap structure itself, we show in Fig. 3 the PES symmetrized at  $E_F$  to remove the spectral cutoff by the Fermi-Dirac distribution. It is now clearly recognized that the intensity at  $E_F$  starts to decrease and gradually forms a gap below 9.5 K. Also in this symmetrized PES which represents the DOS, we cannot discern a well-defined quasiparticle peak. This result is in a striking contrast to that of scanning tunneling spectroscopy (STS) study on a (1 0 0) CVD thin film with  $T_c = 1.9$  K and  $n_B = 1.9 \times 10^{21} \text{ cm}^{-3}$  [18], where a superconducting gap spectrum with well defined quasiparticle peaks ( $\Delta = 0.285$  meV and  $\Gamma = 255$  mK = 0.022 meV at  $T = 70$  mK) is observed. Furthermore, its temperature dependence is well in accord with the weak-coupling BCS gap function with  $\Delta(0) = 1.74k_B T_c$ . On the other hand, another very recent STS result on a (1 1 1) CVD thin film with  $n_B = 6 \times 10^{21} \text{ cm}^{-3}$  and  $T_c^m = 5.4$  K shows a broad superconducting gap spectrum fairly similar to ours with  $\Delta = 0.87$  meV and  $\Gamma = 0.38$  meV at 0.47 K [19]. Both measurements report that the STS spectra reflecting the local DOS show very little dependence on the location at the sample surfaces, which should rule out the possibility of mesoscopic (nanoscale) modification of the superconducting state in these samples. The discrepancy among the results on (1 0 0) and (1 1 1) samples may be explained by the difference in  $n_B$ . We note that on increasing  $n_B$ , the mobility tends to get lower reflecting the disorder induced by random boron doping. Recent ARPES result also shows that the lifetime of the carriers estimated from the spectral linewidth becomes shorter in the sample with higher  $n_B$  [8]. They indicate the possible dirtiness of the electronic structure in high- $n_B$  samples, which gives rise to the superconducting gap with large  $\Gamma$  as observed in (1 1 1) samples. Another possibility is the extrinsic sample inhomogeneity which is known to be greater in (1 1 1) samples. It is actually reported that there are two structural phases with slightly different lattice constants in (1 1 1) samples when  $n_B$  and  $T_c$  become high ( $T_c^m > 6$  K) [20]. Since the lattice constant of a heavily B-doped diamond is greater than that of undoped ones by about 0.5%, there is a tendency toward a uniaxially expanded phase near the substrate and an isotropically relaxed phase for the rest. Though exactly how these two phases coexist in BDD thin films is yet under investigation, such local inhomogeneity may account for the lousy superconducting gap structure in our PES result.

Now we discuss the temperature dependence of the superconducting gap in this sample. Since it is very difficult to get accurate gap values by fitting these rather featureless spectra

for all temperatures, we simply estimated the energy shift of the leading edge in PES (Fig. 2) instead. Its temperature dependence in Fig. 4 rather resembles that of the Meissner response which monotonically keeps growing on decreasing temperature, as shown in Fig. 1(b). The onset temperature of gap evolution at around  $T_0 \sim 11$  K, however, is apparently higher than that of the magnetization,  $T_c^m = 6.6$  K. Looking back on the resistivity curve in Fig. 1(a), we find a characteristic behavior at around  $T_0$ . At  $T_0$ , the resistivity starts to deviate from the weakly insulating normal state which is apparent under a magnetic field. Such a deviation may be reflecting the inhomogeneous conductivity near  $T_c$ , which attributes  $T_0$  to the onset of the local superconducting transition and  $T_c^{\text{off}} \sim 7$  K to the temperature of bulk supercurrent percolation. If this is the case, our PES result is suggestive of its high sensitivity that probes the local superconducting state with high  $T_c$ . At the same time, it shows the potential for development of a diamond superconductor with  $T_c \sim 11$  K by aggregating such local “high- $T_c$ ” segments.

In conclusion, we have performed an ultrahigh resolution photoemission spectroscopy measurement to elucidate the near- $E_F$  electronic structure of the superconducting boron-doped diamond with  $T_c^m = 6.6$  K. We observed the gradual formation of the superconducting gap below  $T_0 \sim 11$  K, the temperature where the deviation of the resistivity from the normal state is observed. The dominant size of the gap, though under an uncertainty due to the lack of quasiparticle peak, is estimated to be about  $\Delta = 0.78$  meV at 4.5 K. Its broad spectral shape and the diffusive temperature dependence indicate that the superconductivity in this system is strongly affected by randomness and/or inhomogeneity introduced by boron doping. Further precise investigation is desired using samples with the least extrinsic nonstoichiometry.

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FIG. 1: (color online). Temperature dependence of the resistivity (a) and the magnetization (b) in B-doped diamond. Insets show the magnification of the temperature regions near the superconducting transition.  $T_0$  shows the temperature where the resistivity starts to deviate from the normal state behavior, whereas  $T_c^m$  represents the onset temperature of the Meissner response.

FIG. 2: (color). Temperature dependence of the ultrahigh resolution photoemission spectrum in the B-doped diamond (a). Enlarged plot around  $E_F$  is shown in (b). (c) shows the PES at 4.5 K indicated together with the fitting result.

FIG. 3: (color online). Temperature dependence of PES in B-doped diamond symmetrized at  $E_F$  to exclude the Fermi-Dirac cutoff.

FIG. 4: (color online). Temperature dependence observed in the energy shift of the leading edge in PES (Fig. 2), which should reflect that of the superconducting gap.  $T_0$  and  $T_c^m$  indicate the characteristic temperature observed in resistivity and magnetization, respectively (see Fig. 1). Broken curve is merely a guide-for-eyes.



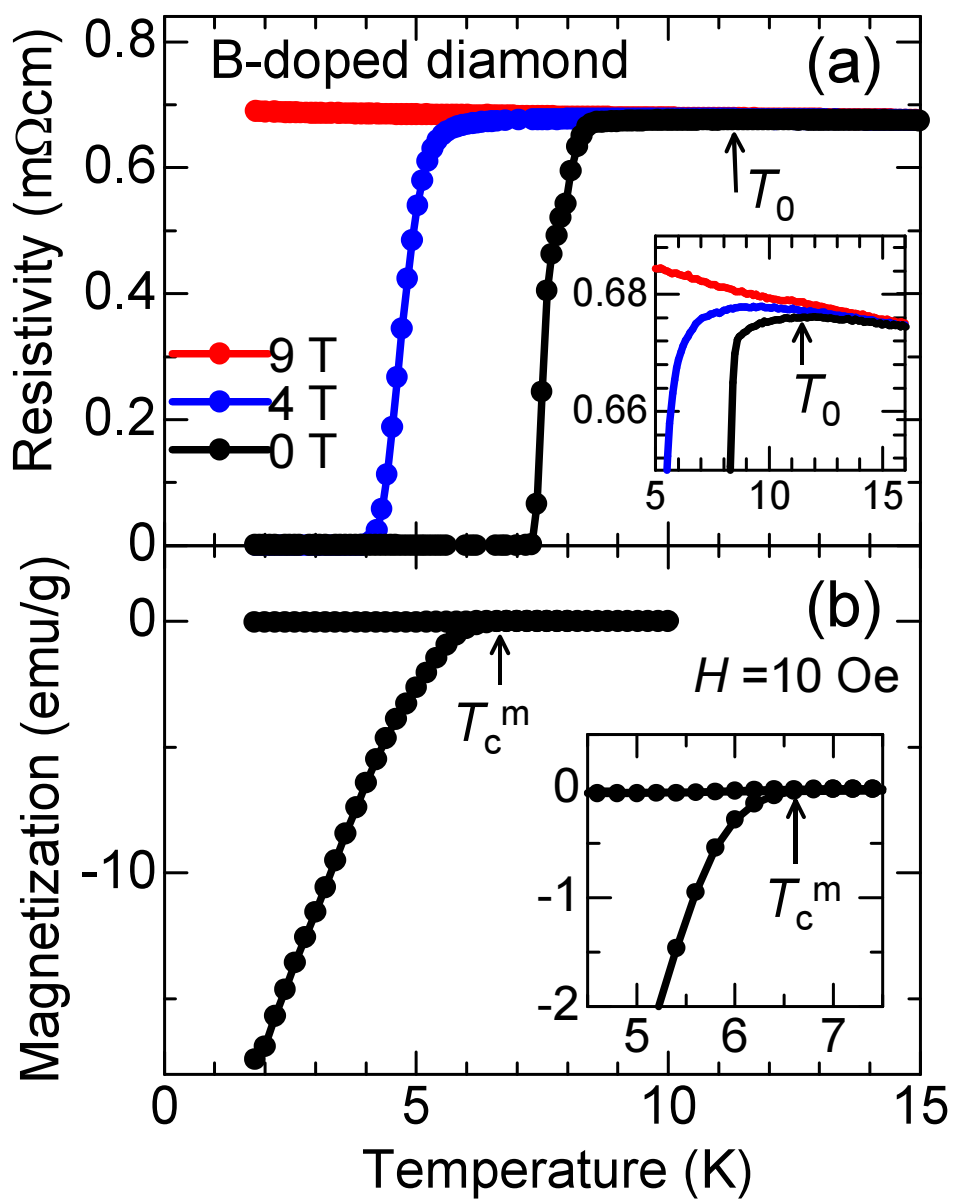


Figure 1 (K. Ishizaka et al.)

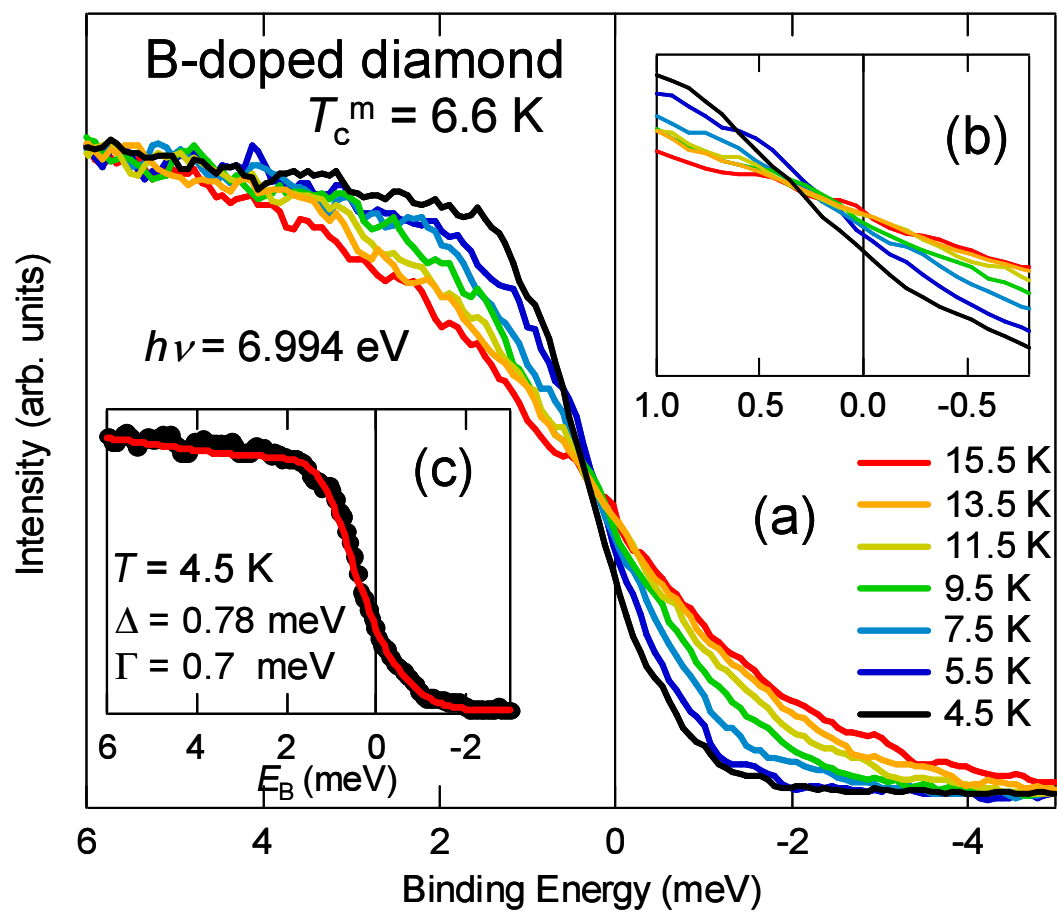


Figure 2 (K. Ishizaka et al.)

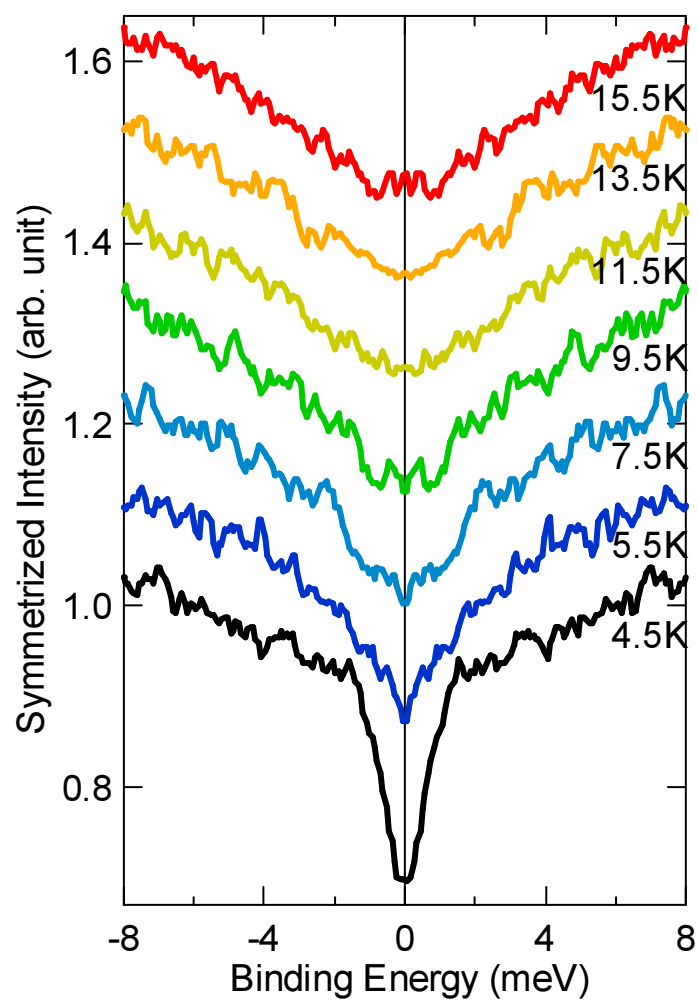


Figure 3 (K. Ishizaka et al.)

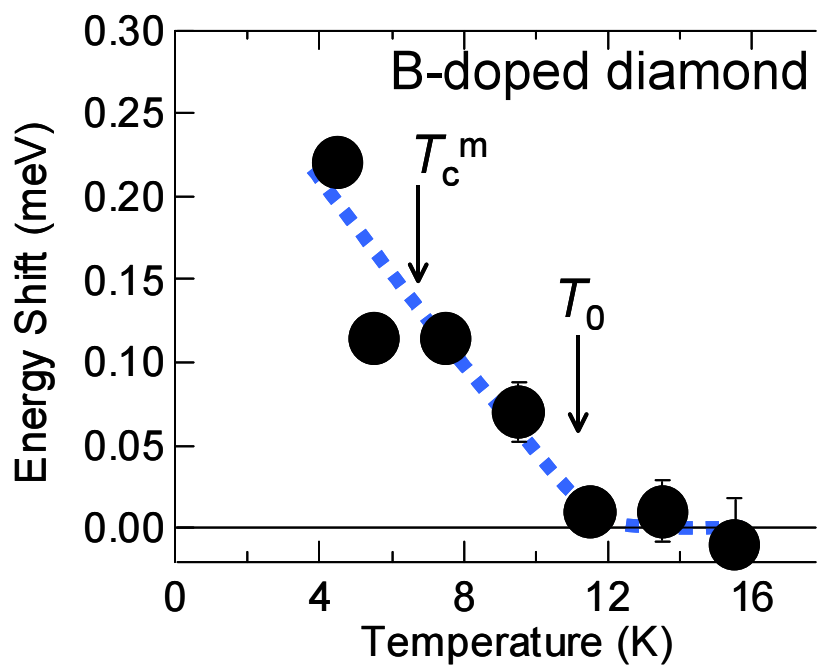


Figure 4 (K. Ishizaka et al.)